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(54) Title: POLYMER PREPARATION (54) Titre: PREPARATION DE POLYMERES (57) Abstract <p>A process for preparing a conjugated polymer, which comprises polymerizing in a reaction mixture (a) an aromatic monomer having at least two reactive boron derivative groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one reactive boron derivative group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a palladium catalyst, and an organic base in an amount sufficient to convert the reactive boron derivative groups into $-B(OH)_2$ anions.</p> (57) Abrégé <p>L'invention concerne un processus de préparation d'un polymère conjugué, qui consiste à polymériser dans un mélange réactionnel (a) un monomère aromatique possédant au moins deux groupes dérivés de bore réactif d'un groupe d'acide borique, un groupe d'ester borique et un groupe de borane, et un monomère aromatique possédant au moins deux groupes fonctionnels haloïdes; ou (b) un monomère aromatique possédant un groupe fonctionnel d'halogénure réactif et un groupe dérivé de bore réactif d'un groupe d'acide borique, un groupe d'ester borique et un groupe de borane. Ce mélange réactionnel comprend une quantité catalytique d'un catalyseur au palladium, et une base organique en quantité suffisante pour convertir les groupes dérivés de bore réactif en anions $-B(OH)_2$.</p>		

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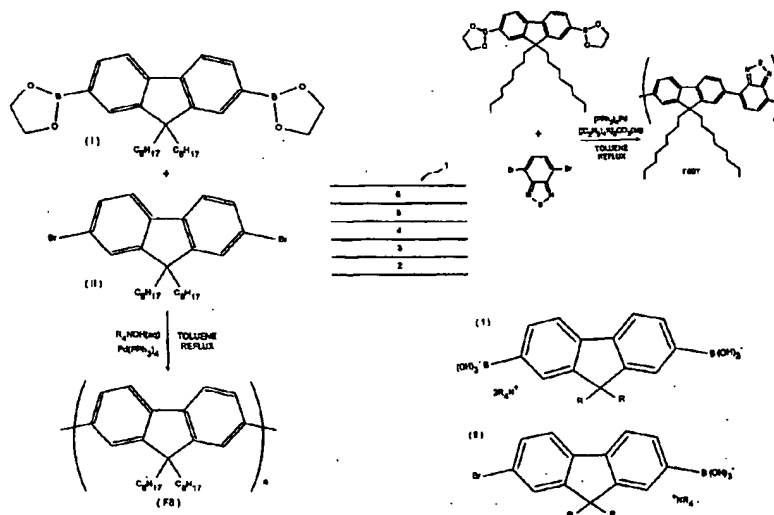
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(71) Applicant (for all designated States except US): CAMBRIDGE DISPLAY TECHNOLOGY LIMITED [GB/GB]; Greenwich House, Madingley Rise, Madingley House, Cambridge CB3 0HJ (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): TOWNS, Carl, Robert [GB/GB]; 193 Silver Street, Crown Cottage, Mountfitchet, Stansted, Essex CM24 8HB (GB). O'DELL, Richard [GB/GB]; 53 Bearton Green, Hitchin, Herts SG5 1UL (GB).			
(74) Agents: DANIELS, Jeffrey, Nicholas et al.; Page White & Farrer, 54 Doughty Street, London WC1N 2LS (GB).			

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(54) Title: POLYMER PREPARATION



(57) Abstract

A process for preparing a conjugated polymer, which comprises polymerizing in a reaction mixture (a) an aromatic monomer having at least two reactive boron derivative groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one reactive boron derivative group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a palladium catalyst, and an organic base in an amount sufficient to convert the reactive boron derivative groups into $-B(OH)_3^-$ anions.

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Description

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POLYMER PREPARATION

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The present invention relates to a process for preparing a polymer such as a conjugated polymer for use in an optical device such as an electroluminescent device.

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Organic electroluminescent devices are known which employ an organic material for light emission. For example, WO90/13148 describes such a device comprising a semiconductor layer comprising a polymer film which comprises at least one conjugated polymer situated between electrodes. The polymer film in this case comprises a poly(para-phenylene vinylene) (PPV) film which is capable of light emission when electrons and holes are injected therein. Other polymer layers capable of transporting holes or transporting electrons to the emissive layer may be incorporated into such devices. The bandgap of PPV and other poly(arylene vinylene) polymers may be tuned to modulate the wavelength, quantum efficiency and/or refractive index thereof, as described in EP-A-0544795.

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Preparation of poly(arylene vinylene)s for use in optical devices has been conveniently carried out by a precursor route where thermal elimination of leaving groups gives rise to a conjugated polymer, or by other routes such as a dehydrohalogenation reaction. However, poly(arylene vinylene)s are not the only class of polymers which are suitable for use in optical devices. Other aryl-containing polymers may be useful and one route generally useful in the production of conjugated polymers is the Suzuki reaction (Synthetic Communications 11(7), 513, 1981). This reaction involves the use of a palladium-based catalyst, an aqueous alkaline carbonate or bicarbonate inorganic base

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5 and a solvent for the reactants and possibly the polymer product. The monomer reactants are typically a diboronic acid or diboronate monomer and a dibromo monomer.

10 US 5777070 is directed to attempts to improve the Suzuki reaction to form conjugated polymers from aromatic monomers. US 5777070 indicates that such reactions require
15 as a solvent a non-polar solvent such as toluene. However, such non-polar solvents are acknowledged to slow down the rate of reaction. In order to overcome this disadvantage,
20 US 5777040 proposes the use of a phase-transfer catalyst such as tricaprylmethyl ammonium chloride sold under the registered trade mark Aliquat to increase the rate of
25 reaction. Accordingly, the reaction mixture contains an organic solvent such as toluene, an aqueous solution of an inorganic base such as sodium bicarbonate, a catalytic amount of a palladium complex and a catalytic amount of the
30 phase transfer catalyst.

The inventors of the present invention have identified a
35 number of drawbacks with the process described in US 5777070. Firstly, the reaction is very slow; reaction times are typically of the order of 18 hours in order to produce a polymer having a molecular weight of the desired
40 order. Discolouration of the polymer product and decomposition of the catalyst become concerns with such long reaction times. Secondly, the reproducibility of the reaction is somewhat poor. The monomer ratio is generally
45 used in the case of copolymerization to control the molecular weight of the product polymer. However, the present inventors have noticed that the peak molecular weight of polymers produced according to the method
50 disclosed in US 5,777,070 vary considerably from reaction

5 to reaction even when the starting monomer ratio is the
same. Experiments conducted by the inventors of the present
invention have shown that the peak molecular weight of the
10 product polymer can vary by as much as about 100,000 for
the same starting monomer ratio. Thirdly, the inventors of
the present invention have also noticed that significant
foaming is observed and that side products are produced
15 which complex strongly to the walls of the reaction vessel,
when a glass reaction vessel is used. These are difficult
to remove, and the reaction thus requires the use of
specialized reaction vessels. The above problems also make
20 this a very difficult and expensive process to scale up.

25 The present invention aims to overcome at least some of the
drawbacks mentioned above.

30 According to a first aspect of the present invention,
there is provided a process for preparing a conjugated
polymer, which comprises polymerizing in a reaction mixture
(a) an aromatic monomer having at least two boron
derivative functional groups selected from a boronic acid
35 group, a boronic ester group and a borane group, and an
aromatic monomer having at least two reactive halide
functional groups; or (b) an aromatic monomer having one
reactive halide functional group and one boron derivative
40 functional group selected from a boronic acid group, a
boronic ester group and a borane group, wherein the
reaction mixture comprises a catalytic amount of a catalyst
suitable for catalysing the polymerisation of the aromatic
45 monomers, and an organic base in an amount sufficient to
convert the boron derivative functional groups into $-B(X)_3^-$
anionic groups, wherein X is independently selected from
50 the group consisting of F and OH.

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The polymerisation proceeds by the coupling of the monomers via elimination of a reactive halide group and a boronate anionic group ($-B(X)_3^-$).

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According to one embodiment of the invention, the conversion of the boron-derivative functional groups to the boronate anionic groups ($-B(X)_3^-$) by the organic base to form a salt having an organic cation is carried out under non-polymerisation conditions prior to polymerisation.

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The boronate anionic group has the formula $-B(OH)_nF_m^-$, wherein $n+m=3$ and n and m are each 0, 1, 2 or 3. The boronate anionic group is preferably a $-B(OH)_3^-$ group. However, the reaction may also proceed, for example, via a $-B(OH)_2F^-$ anionic group using, for example, a tetraalkylammonium fluoride as the organic base.

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The term conjugated polymer refers to either a fully conjugated polymer i.e. a polymer which is conjugated along the full length of its chain, or a partially conjugated polymer i.e. a polymer which contains conjugated segments together with non-conjugated segments.

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The term aromatic monomer refers to any monomer which has the respective functional groups directly substituted on one or more aromatic rings. In the case of monomers having more than one aromatic ring, the functional groups can be substituted on either the same or different aromatic rings. Examples of suitable types of monomers include, but are not limited to, arylenes, heterocyclic aromatic monomers, and fused aromatic systems such as biphenylenes, naphthalenes and fluorenes. Each monomer preferably comprises an

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5 arylenes, a heteroarylene, a triarylamine, or a bisarylene
vinylene. Each aromatic group within the monomer may be
substituted or unsubstituted. Particularly preferred types
10 of monomers include dialkylphenylenes, dialkoxy phenylenes,
substituted and non-substituted thiophenes and
benzothiadiazoles, and dialkylfluorenes such as 9,9-di-n-
15 octylfluorenes. One or more of the monomers could also be
a pre-formed oligomeric or polymeric chain comprising
several smaller units with the necessary functional groups
provided at the desired positions on the chain.

20 It is also envisaged that under the appropriate reaction
conditions, this invention could also be extended to the
use of monomers in which some or all of the functional
25 groups are not directly substituted on an aromatic ring, in
particular to other kinds of unsaturated monomers.

30 Monomers particularly useful in the present invention
include those which may be polymerised to form a
semiconductive conjugated polymer such as a semiconductive
conjugated polymer for use in an optical device such as an
35 electroluminescent device. Such polymers may be used in an
emissive layer or as a hole transport or electron transport
polymer. Luminescent polymers are particularly useful in
such devices. The conjugated polymer may be fully or
40 partially conjugated, perhaps containing conjugated
segments and may be a homopolymer, a copolymer or an
oligomer, and may be a linear or a branched chain polymer
such as a dendrimer.
45

As described above, the monomers must each have the
appropriate functional groups for the Suzuki reaction. In
50 one arrangement, a first reactive dihalide monomer is

5 polymerised with a second monomer having two boron
derivative functional groups. In this arrangement the
first and the second monomers may be the same or different.
10 Where the monomers are the same, a homopolymer is produced.
Where the monomers are different, a copolymer is produced.
In a second arrangement, a monomer having a boron
derivative functional group and a reactive halide
15 functional group is polymerised to form a homopolymer. It
is also possible to form copolymers from this second
arrangement simply by polymerising together two or more
different types of monomers each containing both
20 functionalities.

25 Preferably, the reactive halide functional group on the
reactive dihalide monomer or the monomer having the
reactive halide functional group is Br or I although it is
possible to use instead groups such as chlorine, triflate
30 (CF_3SO_3^-), tosylate and mesylate.

With respect to the boron-derivative functional groups, the
boronic acid group is represented by $-\text{B}(\text{OH})_2$; the boronic
35 ester group is preferably $-\text{B}(\text{OR}^1)(\text{OR}^2)$ or $-\text{B}(\text{OR}^5\text{O})$ and the
borane group is preferably $-\text{BR}^3\text{R}^4$, wherein R^1 is a
substituted or non-substituted $\text{C}_1\text{-C}_6$ alkyl group and R^2 is H
or a substituted or non-substituted $\text{C}_1\text{-C}_6$ alkyl group; R^3
40 and R^4 are each independently substituted or non-
substituted $\text{C}_1\text{-C}_6$ alkyl groups, and R^5 is a substituted or
non-substituted divalent hydrocarbon radical resulting in a
5 or 6 membered ester ring. Examples of suitable groups as
45 R^5 include substituted or non-substituted C_2 or C_3 alkylene
groups, or substituted or non-substituted ortho- or meta-
phenylene groups.

5 Suitable boronic ester groups include, for example, the
products of esterification of the corresponding boronic
10 acid group with monovalent C₁-C₆ alcohols, ethane diols
such as pinacol, propane diols or ortho aromatic diols such
as 1,2-dihydroxybenzene.

15 The term "organic base" includes sources of hydroxyl ions
and Lewis bases such as those which create a source of
hydroxyl ions in combination with water. The organic base
20 should be soluble in an organic solvent and/or an aqueous
solvent. It is preferable to deliver the organic base in
the form of an aqueous solution thereof, as this is
effective at hydrolysing boronic ester or borane groups to
25 the corresponding boronic acid groups and then converting
the boronic acid groups to boronate anionic groups.

30 A single organic base or a mixture of different organic
bases may be used.

35 Examples of organic bases include alkyl ammonium
hydroxides, alkyl ammonium carbonates, alkyl ammonium
biscarbonates, alkylammonium borates, 1,5-
diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-
diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-
40 diazabicyclo[2.2.2]octane (DABCO), dimethylaminopyridine
(DMAP), pyridine, trialkylamines and alkylammonium
fluorides such as tetraalkylammonium fluorides.

45 The organic base used in the method of the present
invention is preferably a tetraalkyl ammonium hydroxide
such as tetramethyl ammonium hydroxide, tetraethyl ammonium
hydroxide or tetra-n-propyl ammonium hydroxide.
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In another preferred embodiment of the present invention, a tetraalkyl ammonium carbonate or a tetraalkyl ammonium bicarbonate is used as the organic base. Other preferred

10 bases are tetraalkylammonium borates, particularly, tetraethylammonium borate. These bases are particularly useful for reducing monomer degradation.

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The most suitable organic base for any given system will depend on the nature of the monomers and solvent system employed. For example, in the case of the preparation of

20 polyfluorenes from the boronic ester using toluene as a solvent, a base selected from the group of tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide or tetraisopropyl ammonium hydroxide is particularly

25 preferred, with tetraethyl ammonium hydroxide being the most preferred of these organic bases.

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The quantity of the base will depend on various factors such as the type of particular base used and the type of boron derivative functional group used. However, it has to be present in a sufficient quantity to convert the boron

35 derivative functional group into the corresponding $-B(X)_3^-$ anionic group, which is the reactive species which is eliminated with the reactive halide functional group to effect polymerisation. In the case that the boron-

40 derivative group is a boronic ester or a borane, the organic base should preferably be used in the form of an aqueous solution to provide sufficient water to hydrolyze

45 the boronic ester or borane groups to the corresponding boronic acid groups and convert the boronic acid groups into boronate anionic groups.

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5 The use of one equivalent of organic base per boron-
derivative functional group has been found to give fair
degrees of polymerisation over a relatively long period of
10 time. Preferably, at least 1.5 molar equivalents, further
preferably at least 2 molar equivalents, of the organic
base per boron-derivative functional group are used. For
example, molecular weights over 200,000 have been obtained
15 in a relatively short period of time using 2.26 mole
equivalents of organic base per boron-derivative functional
group.

20 The number of equivalents is defined by the functionality
of the base multiplied by the molar ratio of base to boron-
derivative functional groups.

25 It is preferable that the reaction mixture includes a
solvent in which the conjugated polymer is soluble. For
example, in the case of polyfluorenes, non-polar aromatic
30 solvents such as anisole, benzene, ethylbenzene,
mesitylene, xylene, and particularly toluene are preferred.
It is also preferable that the reaction mixture includes a
solvent in which the organic cation boronate salt produced
35 by the reaction of the organic base with the boron-
derivative functional groups, is soluble.

40 In the case that the boron-derivative functional group is a
boronic ester or borane group, the reaction mixture should
include sufficient water to hydrolyze the boronic ester or
borane group to the corresponding boronic acid group. The
45 organic base, such as a tetralkylammonium hydroxide or
tetraalkyl ammonium carbonate or bicarbonate is preferably
added to the reaction mixture in the form of an aqueous
50 solution to thereby provide sufficient water to hydrolyze

5 the boronic ester or borane groups to the corresponding
boronic acid groups. According to one possible variation,
it is envisaged that the alkyl ammonium hydroxide may
10 alternatively be added in the form of a hydrated salt
thereof such as the trihydrate.

15 It is preferable to carry out the polymerisation in a
single liquid phase by using an organic solvent or solvent
mixture in which all the reaction components, i.e. the
boronate salt produced by the reaction of the organic base
20 with the boron-derivative functional groups and the
dihalide monomers where applicable, are soluble, and with
which water present for hydrolysis of boronic ester groups
or borane groups is miscible.

25 In one embodiment, the reaction mixture further comprises
an aqueous solution of an inorganic base, preferably an
inorganic base which does not include alkali metal ions,
30 such as NH_4OH . This is preferred from the point of view of
producing polymers of particularly high molecular weight.

35 The catalyst used in the method of the present invention is
preferably a palladium catalyst. The palladium catalyst
may be a $\text{Pd}(0)$ complex or a $\text{Pd}(\text{II})$ salt. The $\text{Pd}(0)$ complex
is preferred, a $\text{Pd}(\text{Ph}_3\text{P})_4$ catalyst being particularly
40 preferred. Typically, the amount of palladium catalyst in
the reaction mixture is 0.01 to 1 mol.%, preferably about
0.15 mol.%, based on the total number of moles of monomers
used.

45 The inventors of the present invention have unexpectedly
found that by conducting the reaction using an organic base
50 rather than an inorganic base as in US 5,777,070, the

5 polymerization can be carried out with faster reaction
times and with better reproducibility. They have also
found that the use of an organic base eliminates the
10 problem of foaming and the problem of side-products
becoming strongly complexed to the walls of the reaction
vessel, whereby the need to utilize specialized reaction
15 vessels is eliminated. In addition, the fact that alkali
carbonates or alkali bicarbonates are not required for the
reaction also has the additional advantage that it
eliminates the need for a final purification step to remove
20 alkali metal contaminants, which would otherwise be
required to avoid such contaminants detrimentally affecting
the performance of the polymer material in many
applications. Furthermore, the present inventors have
25 found surprisingly that polymers prepared by this route
have lower residual levels of palladium compared to
polymers prepared by prior art processes. This is
particularly important in the case that the polymer is to
30 be used in a light-emitting device, since the presence of
palladium is believed to have a detrimental effect on the
optical performance of the device.

35 Furthermore, in the process of the present invention, the
molecular weights grow gradually with time in these very
controlled polymerisations. This has the advantage that
40 repeatable (consistent) and desired molecular weights can
be achieved by stopping the reaction at the appropriate
stage.

45 In a fourth aspect, the present invention provides a
process for the production of an optical device or a
component for an optical device. The process comprises
50 providing a substrate and producing a polymer in accordance

5 with the process as described above, whereby the polymer is supported by the substrate. The polymer may be supported by the substrate directly, for example where a polymer film is deposited or formed on the substrate, typically a transparent substrate. Alternatively, the polymer may be supported by the substrate indirectly where one or more intervening layers between the substrate and the polymer are provided. The optical device may comprise a luminescent device such as an electroluminescent device in which the polymer is disposed between a cathode and an anode. Where the polymer is an emissive layer, a hole transport layer may be provided between the anode and the substrate and an electron transport layer may be provided between the polymer and the cathode.

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The present invention will now be described in further detail, by way of example only, with reference to the accompanying drawings, in which:

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FIGURE 1 shows a reaction scheme in accordance with the invention;

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FIGURE 2 shows a schematic representation of an optical device according to the invention;

FIGURE 3 shows another reaction scheme in accordance with the present invention; and

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FIGURE 4 shows examples of the boronate anions by which the polymerisation proceeds.

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Figure 1 illustrates one possible route for providing poly 2,7(9,9-di-n-octylfluorene) (F8 comprising a chain of di-n-octyl fluorene repeating units. A 2,7(9,9-di-n-octylfluorene)diboronate (I) is reacted with a corresponding 2,7-dibromo-(9,9-di-n-octylfluorene) (II) in

5 toluene in the presence of a palladium catalyst such as
Pd(PPh₃)₄ and an organic base such as a tetraalkyl ammonium
10 hydroxide, tetraalkyl ammonium carbonate or tetraalkyl
ammonium bicarbonate to produce polymer F8.

15 In an alternative embodiment of the present invention, this
polymer can be produced by, for example, the
homopolymerization of 2-bromo-(9,9-di-n-octylfluorene)-7-
ethylenylboronate in toluene in the presence of a palladium
catalyst and an organic base.

20 Example 1

25 Polymer F8 was produced according to the following method.
A three-necked 500ml round bottomed flask fitted with a
glass stirring rod attached to an electrical mechanical
stirrer, a Teflon stirring blade, and a reflux condensor
30 (connected to a nitrogen line) was charged with 9,9-
dioctylfluorene-2,7-di(ethylenylboronate) (4.773g,
9.0mmol), 2,7-dibromo-9,9'-dioctylfluorene (4.936g,
9.0mmol), tetrakis-(triphenylphosphine)palladium (31.2mg,
35 0.027mmol) and toluene (90ml). The solution was stirred
under nitrogen at room temperature for approximately ten
minutes. An aqueous solution of tetraethyl ammonium
40 hydroxide (30ml, 20% wt/vol.) was added to the stirring
mixture at room temperature.

45 The stirring mixture was heated to and maintained at reflux
(115°C oil bath temperature) for approximately two hours.
Bromobenzene (1-2ml) was added to the mixture, which was
allowed to stir at reflux for a further hour before adding
50 phenyl boronic acid (1.5-2.0g), after which the mixture was
allowed to stir at reflux for one hour.

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The mixture was allowed to cool to room temperature and poured slowly into 4 litres of methanol to precipitate the polymer. The polymer/methanol mixture was then filtered. The polymer isolated by filtration was then further reprecipitated into methanol from toluene solution.

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The polymer obtained by this method had a peak molecular weight of 204,000. This and other molecular weights given below were measured using the Polymer Labs GPC system incorporating an LC1120 isocratic pump and ERC-7515A Refractive Index Detector. The solvent used was THF at a flow rate of 1mL/min, and the temperature was controlled at 35°C. The column type was PL mixed (*2, 30cm) calibrated using PL 600-500000 polystyrene standards.

Example 2

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Polymer F8 was produced in exactly the same way as in Example 1 except that the aqueous solution of tetraethyl ammonium hydroxide was added dropwise. The polymer obtained had a peak molecular weight of 229,000.

Example 3

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Polymer F8 was produced in exactly the same way as in Example 1 except that the reaction was carried out at half-scale in a 250ml flask. The polymer obtained had a peak molecular weight of 222,000.

Example 4

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5 Polymer F8 was produced in exactly the same way as in
Example 1 except that an aqueous solution of ammonium
10 hydroxide (10.45ml ammonium hydroxide made up to 20ml with
water) was further added to the monomer and toluene mixture
prior to stirring under nitrogen at room temperature for
15 ten minutes. No reaction was observed until the aqueous
solution of tetraethyl ammonium hydroxide was added. The
polymer obtained had a peak molecular weight of 373,650.

20 Example 5

Polymer F8 was produced in exactly the same manner as in
Example 1 except that an aqueous solution of an identical
25 molar quantity of tetramethyl ammonium hydroxide was used
instead of the aqueous solution of tetraethyl ammonium
hydroxide. The polymer obtained had a peak molecular
weight of 150,500.

30 Example 6

Polymer F8 was produced in exactly the same way as in
35 Example 1 except that an aqueous solution of an identical
molar quantity of tetrapropyl ammonium hydroxide was used
instead of the aqueous solution of tetraethyl ammonium
hydroxide. The polymer obtained had a peak molecular weight
40 of 142,000.

45 Example 7

The reaction scheme for the synthesis of F8BT polymer using
Bis(tetraethylammonium)carbonate as base is shown in Figure
3.
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5 A 500ml reaction vessel was charged with 9,9-
dioctylfluorene-2,7-diethylenyl (4.773g, 9.0 mmol.),
10 2-7-dibromobenzothiadiazole (2.6449g 9.0 mmol,
tetrakis(triphenylphosphine) palladium 31.2 mg, and toluene
100 ml. The mixture was stirred at room temperature for 10
minutes under nitrogen. Bis(tetraethylammonium)carbonate
15 (13.0g) dissolved in 20 ml of de-ionised water was then
added to the mixture, which was then allowed to stir at
room temperature under flow of nitrogen for 20 minutes.

20 The reaction mixture was heated to and maintained at reflux
under nitrogen for up to 18 hours (typically left
overnight). During this time the reaction mixture was
stirred (setting rate 2-3) under an atmosphere of nitrogen.

25 Bromobenzene (1 ml) was then added and the reaction mixture
allowed to stir at reflux for 2 hours, after which phenyl
boronic acid was added (2 g) and the reaction mixture was
30 allowed to stir at reflux for a further 2 hours.

35 The mixture was allowed to cool to room temperature and
poured into 4 l of methanol to precipitate the polymer.
The polymer/methanol mixture was then filtered and the
polymer was allowed to air dry on the Buchner funnel for
40 five minutes. Aluminium foil was used to cover the top of
the Buchner funnel to minimise light exposure.

45 After purification, the final yield was ~3.05 g, 64%. The
peak molecular weight was found to be 175,000 (Mp) as
determined by GPC.

50 Example 8

5 A further synthesis was carried out in accordance with the
synthesis described in Example 7 except that, in this
particular case a mixed solvent system was used
10 (THF/toluene) (~50:50). The molecular weight obtained was
~350,000 (Mp).

15 Example 9

9,9-di-n-octylfluorene-2,7-di(ethyleneboronate), 2,7-
20 dibromo-9,9-di-n-octylfluorene and a palladium catalyst
such as tetrakis(triphenylphosphine)palladium are dissolved
in tetrahydrofuran (THF). To this is added two equivalents
of a tetraalkylammonium hydroxide as an aqueous solution of
25 concentration at least 20% by weight. The mixture is
stirred at room temperature under a flow of nitrogen for 20
min. During this time, the tetraalkylammonium disalt shown
as (1) in Figure 3 is formed and dissolves in the THF with
30 the other components to give a clear single liquid phase.
The reaction is heated to the reflux temperature of THF
(66°C) during which time the solution viscosity increases
as polymer molecular weight increases. The reaction is
35 usually complete within two hours.

As demonstrated above, particularly good results have been
40 achieved in this polymerisation by using a polar organic
solvent in which the boronate salt and the dihalide
monomers are soluble and which is miscible with water
(tetrahydrofuran) to provide a single phase reaction
45 mixture. The polymerisation can be carried out at a
relatively low temperature and in a relatively short period
of time. Furthermore, relatively high molecular weights
50 can be achieved. The use of lower reaction temperatures

5 and shorter reaction times has the added advantage that there is little if any palladium catalyst decomposition.

10 Example 10

15 9,9-di-n-octylfluorene-2,7-di(ethyleneboronate), 2,7-dibromo-9,9-di-n-octylfluorene and a palladium catalyst such as tetrakis(triphenylphosphine)palladium are dissolved in a mixture of toluene and THF (e.g. 1:1 mixture). To
20 this is added two equivalents of a tetraalkylammonium hydroxide as an aqueous solution of concentration at least 20% by weight. The mixture is stirred at room temperature under a flow of nitrogen for 20 min. During this time, a
25 tetraalkyl ammonium disalt of the kind shown as (1) in Figure 4 is formed as a white solid precipitate suspended in a single liquid phase. The reaction is heated to the reflux temperature of THF (66°C) during which time the
30 solution viscosity increases as polymer molecular weight increases. The reaction is usually complete within two hours.

35 As demonstrated above, this polymerisation can also be carried out in mixtures of water-miscible organic solvents such as THF and non water-miscible non-polar solvents such
40 as toluene. Although the disalt tends to precipitate upon its in-situ formation to give a two phase system, the use of such a solvent mixture can be advantageous as some
45 polymers are more compatible with a polar solvent such as THF whereas others are more soluble in non-polar solvents like toluene. The ability to use such solvent mixtures means that far more polymer types can be prepared without a
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5 risk of premature polymer precipitation during polymerisation.

10 Example 11

15 9,9-di-n-octylfluorene-2,7-di(ethyleneboronate), 2,7-dibromo-9,9-di-n-octylfluorene and a palladium catalyst such as tetrakis(triphenylphosphine)palladium are dissolved in tetrahydrofuran (THF). To this is added two equivalents of a tetraalkylammonium hydroxide as an aqueous solution of concentration at least 20% by weight. The mixture is stirred at room temperature under a flow of nitrogen for 20 min. During this time, a tetraalkyl ammonium disalt of the kind shown as (1) in Figure 4 is formed and dissolves in the THF with the other components to give a clear single liquid phase. All the components required for the polymerisation are present in the single liquid phase. The reaction is heated to the reflux temperature of THF (66°C) during which time the solution viscosity increases as polymer molecular weight increases. After a certain amount of time (e.g. 1 hour) a proportion of a second organic solvent (e.g. toluene) is added and the reaction is continued at the same temperature until further molecular weight increase is not observed (usually a total reaction time of two hours).

40 As demonstrated in this example, good results have also been achieved for this polymerisation by starting with a water-miscible polar organic solvent (THF) as in Example 9, and adding a second miscible organic solvent in which the polymer is soluble as the polymerisation proceeds.

5 The molecular weights grow gradually with time in these
very controlled polymerisations. This has the advantage
10 that repeatable (consistent) and desired molecular weights
can be achieved by stopping the reaction at the appropriate
stage.

15 Comparative Example 1

A three necked 250 ml round bottomed flask fitted with a
glass stirring rod attached to an electrical mechanical
20 stirrer (Heidolph RZH 2020), teflon stirring blade, reflux
condenser (connected to a nitrogen line) was charged with
9,9-dioctylfluorene-2,7-di(ethylenylboronate) (4.8779g,
9.09 mmol, 98.8 % purity by HPLC), 2,7-dibromo-9,9'-
25 dioctylfluorene ((4.9360g, 9.0 mmol) 100 % purity by HPLC))
and toluene (90 ml). The solution was stirred under
nitrogen for a 10 minutes and then 3.5g of a surfactant
solution (10g of Aliquat 336 and Toluene 25g) (2.5mmol
30 Aliquat 336) was added along with 20 ml of 2M solution of
sodium carbonate. The mixture was then stirred at room
temperature under nitrogen for a further 15 minutes. The
35 catalyst, tetrakis(triphenylphosphine)palladium 31.2 mg, was
then added and the reaction mixture was heated and
maintained at reflux for 18 hours.

40 During this time the reaction mixture was stirred (setting
rate 2 -3) under an atmosphere of nitrogen. The reaction
mixture was observed after 2 hours, but there was no sign
45 of any production of the polymer indicating the slowness of
the reaction.

5

After 20 hours bromobenzene (1 ml) was added and the reaction mixture was allowed to stir at reflux for a further 20 hours.

10

The mixture was allowed to cool to room temperature and poured into 4L of methanol to precipitate the polymer. The polymer/methanol mixture was then filtered and the polymer was allowed to air dry on the Buchner funnel for five minutes. Aluminium foil was used to cover the top of the Buchner funnel to minimise light exposure.

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Polymer F8 was produced twice according to the above. The polymers obtained had a molecular weight of 170000 and 230000 ,respectively, showing relatively poor reproducibility.

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Figure 2 shows in a purely schematic way the order of layers in an electroluminescent device generally designated 1. Disposed on substrate 2, which is typically a transparent substrate such as glass, is anode 3 which may be a layer of transparent indium tin oxide. Adjacent layer 2 is hole transporting layer 3, which may be a polyethylene dioxythiophene, on which is disposed emissive layer 4, which may be a polymer according to the present invention. Layer 5 is an organic electron transport layer. Layer 6 is a cathode which may be a lithium aluminium layer.

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Claims

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CLAIMS

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1. A process for preparing a conjugated polymer, which comprises polymerizing in a reaction mixture (a) an aromatic monomer having at least two boron derivative functional groups selected from a boronic acid group, a boronic ester group and a borane group, and an aromatic monomer having at least two reactive halide functional groups; or (b) an aromatic monomer having one reactive halide functional group and one boron derivative functional group selected from a boronic acid group, a boronic ester group and a borane group, wherein the reaction mixture comprises a catalytic amount of a catalyst suitable for catalysing the polymerisation of the aromatic monomers, and an organic base in an amount sufficient to convert the boron derivative functional groups into $-BX_3^-$ anionic groups, wherein X is independently selected from the group consisting of F and OH.

2. A process for preparing a conjugated polymer, which comprises preparing under non-polymerisation conditions an organic cation salt of an aromatic diboronate monomer by the reaction of an aromatic monomer having two boron-derivative functional groups with an organic base in an amount sufficient to convert the boron-derivative groups into boronate anionic groups ($-B(X)_3^-$) wherein X is independently selected from the group consisting of F and OH, and then polymerising the organic cation salt of the aromatic diboronate monomer with an aromatic monomer having two reactive halide functional groups in the presence of a catalyst suitable for catalysing the

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polymerisation by elimination of a halide functional group and a boronate anionic group.

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3. A process for preparing a conjugated polymer, which comprises preparing under non-polymerisation conditions an organic cation salt of an aromatic boronate monomer having a reactive halide functional group and a boronate anionic group ($-B(X)_3^-$) wherein X is independently selected from the group consisting of F and OH, and then polymerising the organic cation salt of the aromatic boronate monomer in the presence of a catalyst suitable for catalysing the polymerisation of the organic cation salt by elimination of a halide functional group and a boronate anionic group.

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4. A process according to any of claims 1 to 3 wherein X is a hydroxyl group.

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5. A process according to any preceding claim wherein at least 1.5 equivalents of said organic base per boron-derivative functional group is provided in the reaction mixture.

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6. A process according to claim 5 wherein at least two equivalents of said organic base per boron-derivative functional group is provided in the reaction mixture.

40

7. A process according to any preceding claim wherein the organic base is selected from the group consisting of tetraalkylammonium carbonates, tetraalkylammonium bicarbonates and alkylammonium hydroxides.

45

8. A process according to claim 7 wherein the organic base comprises $R'R''R'''R''''NOH$, wherein R' is a C_1 - C_6 alkyl group, and R'' , R''' and R'''' are each independently hydrogen atoms or C_1 - C_6 alkyl groups.

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9. A process according to claim 8 wherein the organic base is selected from $(\text{CH}_3)_4\text{NOH}$, $(\text{C}_2\text{H}_5)_4\text{NOH}$ and $(\text{C}_3\text{H}_7)_4\text{NOH}$.

10

10. A process according to any one of claims 1 to 5, wherein the organic base is a tetraalkylammonium carbonate or a tetraalkylammonium bicarbonate.

15

11. A process according to any preceding claim wherein the organic base is used in combination with an aqueous solution of an inorganic base.

20

12. A process according to claim 11 wherein the inorganic base is NH_4OH .

25

13. A process according to any preceding claim wherein the reaction is carried out in the absence of alkali metal cations.

30

14. A process according to any preceding claim, wherein at least one of the aromatic monomers is a 2,7(9,9-di-n-octylfluorene).

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15. A process according to any of claims 1 to 3 wherein a solvent which is miscible with water and in which the reactive components are soluble is used.

16. A process according to any preceding claim wherein the catalyst is a palladium catalyst.

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17. A process according to any preceding claim, wherein the polymerising conditions are such that the polymer produced is a semiconductive conjugated polymer.

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18. A process according to claim 17, wherein the semiconductive conjugated polymer is a luminescent polymer.

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19. A process for the production of an optical device or a component for an optical device, which comprises providing a substrate and producing a polymer in accordance with the process of any one of the

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preceding claims, whereby the polymer is supported by the substrate.

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20. A process according to claim 19, wherein the optical device comprises an electroluminescent device.

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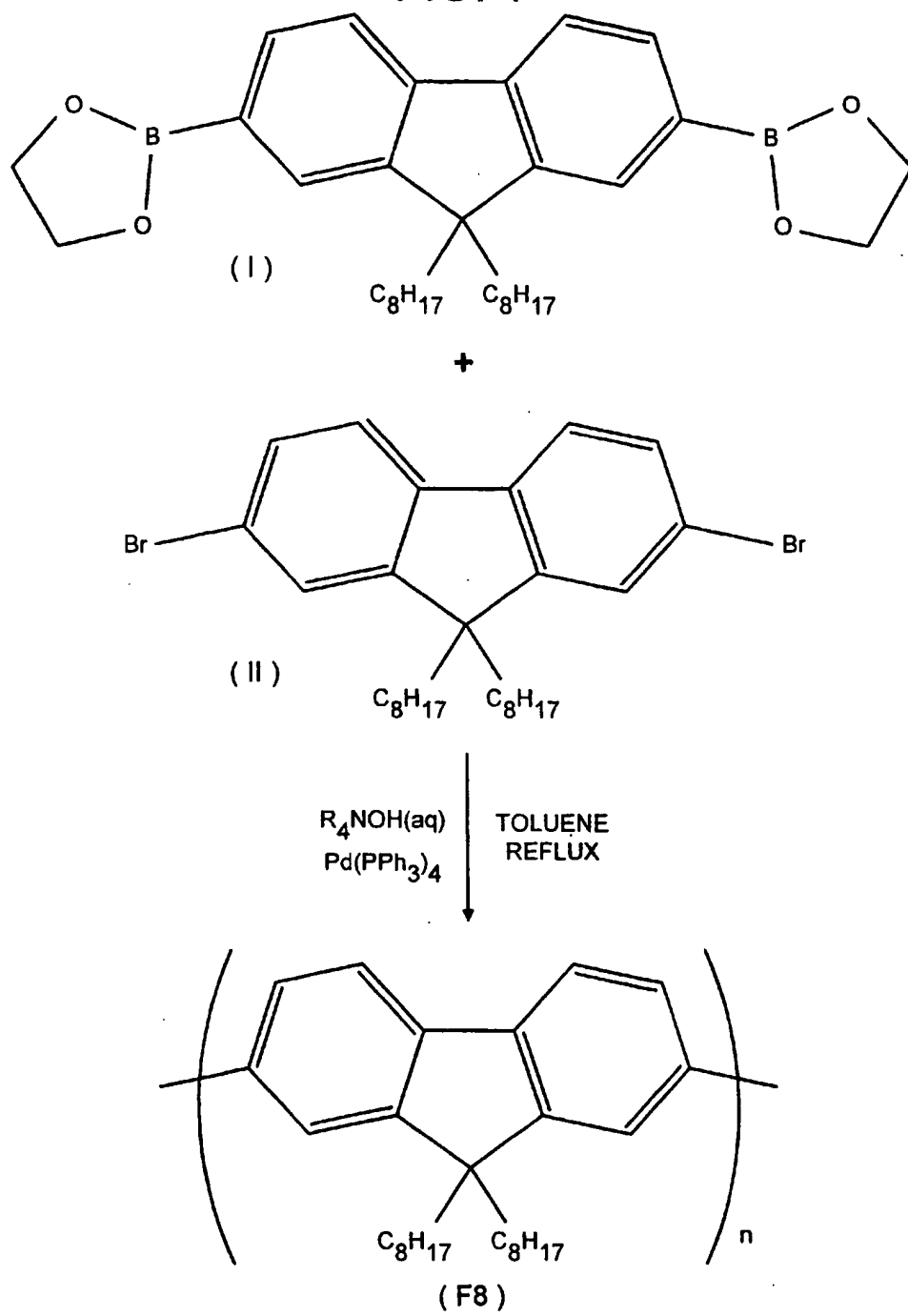
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FIG. 1



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2 / 3

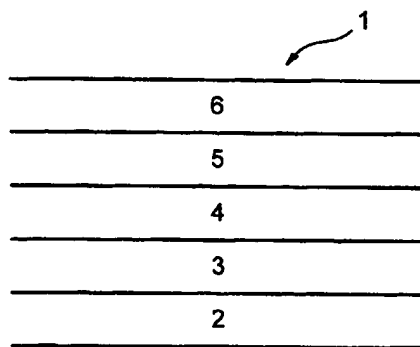


FIG. 2

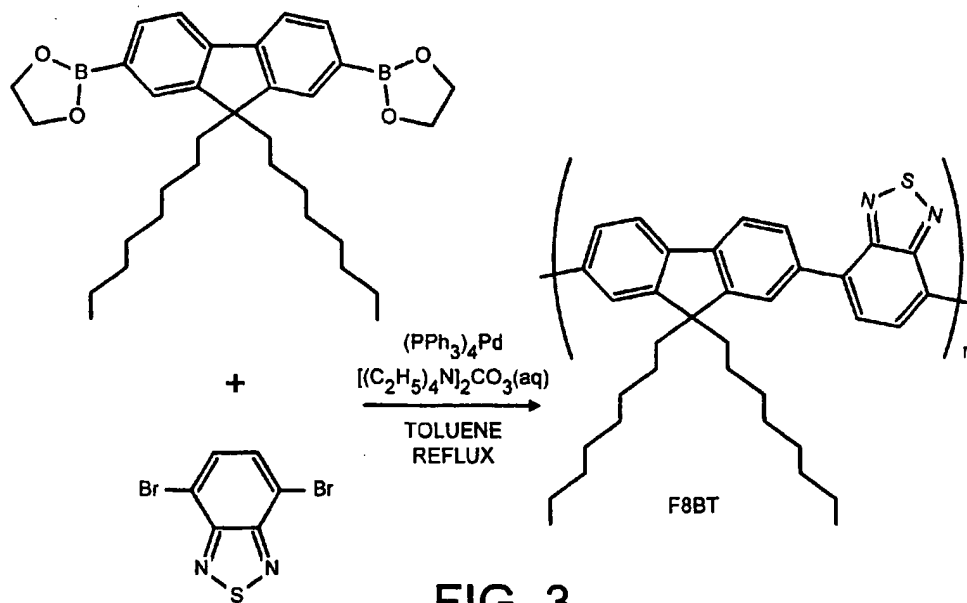


FIG. 3

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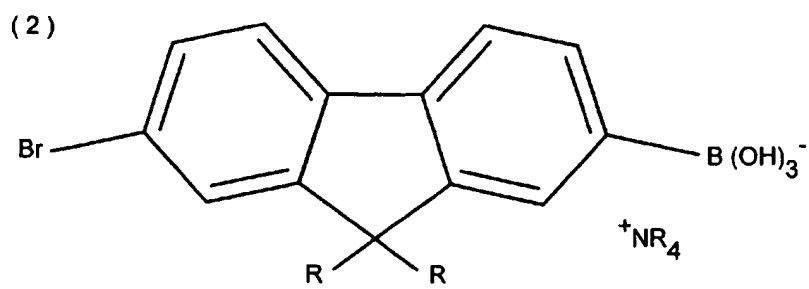
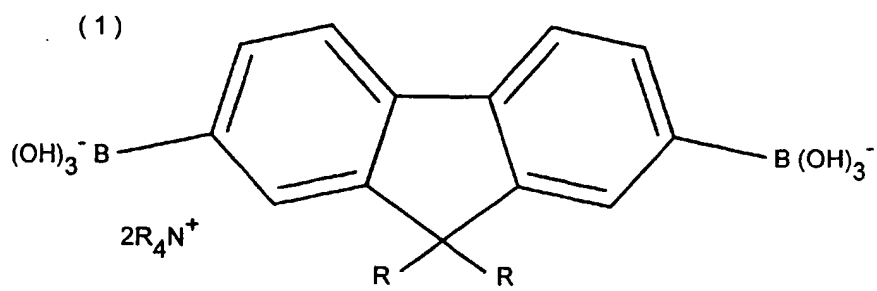


FIG. 4

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/00771

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G61/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 00 22026 A (KREUDER WILLI ; AXIVA GMBH (DE); BECKER HEINRICH (DE); SPREITZER HU) 20 April 2000 (2000-04-20) page 15 page 8, line 18 - line 19	1-6, 13-20
A	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) cited in the application claim 1	1-20
A	DE 42 36 103 A (HOECHST AG) 28 April 1994 (1994-04-28) page 3, line 24 claim 1	1-20
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 May 2000

Date of mailing of the international search report

06/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Paalman, R

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GENET J P ET AL: "Suzuki-Type Cross Coupling Reactions Using Palladium-Water Soluble Catalyst. Synthesis of Functionalized Dienes" TETRAHEDRON LETTERS,NL,ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, vol. 36, no. 9, 27 February 1995 (1995-02-27), pages 1443-1446, XP004028596 ISSN: 0040-4039 page 1444, line 1-3 table 1</p>	1

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